

## *Establishing Energy Scales in High-Temperature Superconductors*

One signature of the onset of superconductivity as the temperature falls below the transition temperature  $T_c$  is the formation of electron pairs. A group of Swedish and Dutch scientists working at the Advanced Light Source (ALS) has used resonant x-ray Raman scattering to investigate electronic transitions between copper 3d states in  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ , an insulating model compound for the copper-based high-temperature superconductors. This compound has a high concentration of copper atoms, making it amenable to detailed study. The researchers found that the transitions have energies that are too high to be directly involved in the pairing mechanism for high-temperature superconductivity, whose identity is one of the great unsolved problems of condensed-matter physics.

The common feature of high-temperature superconductors is their sandwich structure in which the essential ingredient is a set of

parallel copper–oxygen planes. In these planes, each  $\text{Cu}^{2+}$  ion is surrounded by four oxygen atoms. The  $\text{Cu}^{2+}$  ions have nine 3d-electrons in the ten available 3d orbitals, which leaves one 3d orbital unoccupied. One knows from the angular dependence of x-ray absorption that this unoccupied or hole orbital is oriented in the plane with its four lobes pointing towards the four neighboring oxygen atoms, because the electrons are repelled by the negative oxygen ions. In a coordinate system with x and y axes pointing from copper towards oxygen, this orbital is called a  $3d_{x^2-y^2}$  orbital. Owing to quantum-mechanical selection rules, transitions between this and other d states are forbidden by absorption or emission of a single photon and hence are too weak to study. However, resonant Raman scattering is a two-photon process that allows their observation.

The idea is to first excite an electron from the Cu 3p core level

into the empty 3d orbital (Cu  $M_3$  and  $M_2$  resonances near 75 eV) with x ray photons (an allowed transition), and then observe the emitted x rays. If the same electron falls back into the 3p hole that it left behind, it re-radiates the absorbed photon, adding to a large peak in the emission spectrum due to Rayleigh scattering by other electrons. But there is also a significant probability that one of the other 3d electrons falls into the core hole, emitting a photon of a different energy (the Raman scattered photon) in the process and leaving a hole orbital with a different orientation. The net effect is a transition between d states and a reorientation of the hole orbital. The energy difference between the elastic and Raman-scattered photons is then the same as that for the transition between d states. By comparing the intensities emitted normal to the copper–oxygen plane and parallel to the plane, one can deduce the hole's orienta-

tion. The researchers found the xy orbital at 1.35 eV, the xz and yz orbitals at 1.7 eV and the  $z^2$  orbital at 1.5 eV, all of them too far above the ground state to play a direct role in whatever pairing mechanism is operative in the high- $T_c$  superconductors.

Raman spectroscopy with visible light only became routine after the invention of lasers. With the brightness afforded by the ALS, the Swedish/Dutch group has been able to use resonant x-ray Raman spectra for measuring excitation energies that were not known before, thereby shedding light on an important problem in superconductivity. They believe that this technique can be used to address many other problems, such as colossal magnetoresistance, in complex materials dominated by strong Coulomb interactions between electrons (strongly correlated systems).

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P. Kuiper, J.-H. Guo, C. S  the, L.-C. Duda, J. Nordgren, J. J. M. Poethuizen, F. M. F. de Groot, and G. A. Sawatzky, "Resonant X-Ray Raman Spectra of Cu  $dd$  Excitations in  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ ," *Phys. Rev. Lett.* **80** (1998) 5204.

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# RESONANT X-RAY RAMAN SCATTERING OF $\text{Sr}_2\text{CuO}_2\text{Cl}_2$



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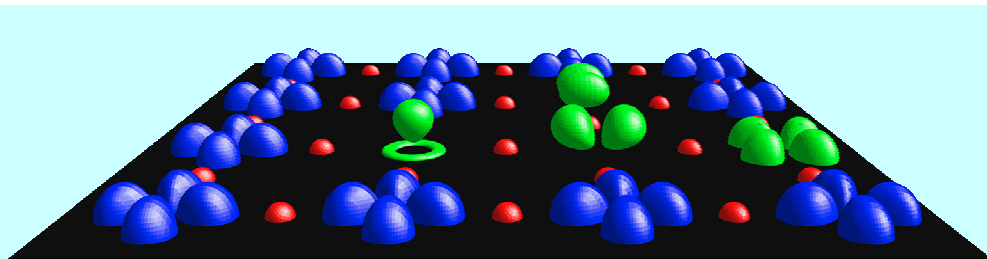
- **High-temperature superconductivity puzzle**
  - *Complicated problem involving strongly correlated electrons*
  - *Mechanism for electron pairing not known*
  - *Conjecture that local dd transitions in copper involved*
- **Resonant Raman x-ray scattering**
  - *Two-photon process allows access to forbidden transitions*
  - *Need bright soft x-ray source*
- **$\text{Sr}_2\text{CuO}_2\text{Cl}_2$** 
  - *Model material for high-temperature superconductivity*
  - *High concentration of copper for strong Raman signal*
  - *Investigate local dd transitions*
- **Polarization-dependent Raman spectra**
  - *Energies of dd transitions*
  - *Orientation of hole orbitals*
  - *Evidence against role of dd transitions in electron pairing*



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*The common feature of high-temperature superconductors is a set of parallel copper–oxygen planes. In these planes, each  $\text{Cu}^{2+}$  ion with d electron orbitals (blue or green) is surrounded by four oxygen atoms (red).*

*The Raman shift and polarization dependence in x-ray resonant Raman spectra give the energies of the transitions and the orientations of the orbitals involved.*

